

## PATENT SPECIFICATION

319,588

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## COMPLETE SPECIFICATION.

## Improvements in Process of Polymerizing Vinyl Derivatives.

We, E. I. DU PONT DE NEMOURS AND Co., a corporation organized and existing under the laws of the State of Delaware, United States of America, located at  
 5 Wilmington, New Castle County, State of Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in methods of polymerising vinyl derivatives. The invention also relates to a  
 15 method of preparing a new polymer of vinyl chloride, namely, a toluene-soluble polymer.

Various methods have hitherto been developed for the polymerisation of vinyl derivatives but all such prior processes involving the use of heat have been difficult to control, especially on account of the exothermic nature of the reaction, and it has therefore been difficult to avoid discoloration or darkening of the polymerised derivatives.

We have now found that it is possible to polymerise vinyl compounds, such as halides or organic esters, as well as hydrocarbon derivatives such as styrene, and by controlling the reaction to prevent the darkening of the polymerised derivative, while at the same time overcoming solubility difficulties with the reactants, prevent damage to the catalyst and permit the entire operation to be effected in the liquid phase. Mixed polymerised esters may be produced in which higher yields than those hitherto obtainable are secured.

It has been proposed to produce resins from crude solvent naphtha containing compounds of the coumarone-indene group by subjecting the naphtha to heat and pressure so as to resinify the  
 45 coumarone-indene constituents, the naphtha being so treated in a continuous autoclave consisting of pipes set within a furnace and within which pipes the pressure is maintained by means of a high pressure pump. Subsequently the product is distilled to remove unchanged and undesirable constituents, the nature of the product depending on the temperature of  
 [Price 1/-].

treatment and distillation. It is stated that the rate of resinification may be increased by the use of strips of copper, silver, gold or platinum which are immersed in the liquid during treatment either in the autoclave or still or during both these steps and act as catalytic agents.

While it is true that solvent naphtha of this kind includes styrolene as a constituent of the coumarone-indene group, and that these coumarone-indene compounds appear to be dissolved in the various solvents, such as xylenes and heavy oils, also present in crude solvent naphtha, it is known that the coumarone-indene compounds polymerise and combine with each other to form compounds of a viscous or resinous character. Such compounds are manifestly different from the polymers obtained from the polymerisation of vinyl derivatives alone or mixed with each other.

In the manufacture of vinyl compounds it has been proposed to react acetylene and a halogen hydride under heat and pressure without the use of catalysts and by increasing the pressure and/or the temperature or time of reaction to produce the polymerisation products thereof, without separating the initially formed vinyl derivatives.

According to the present invention the improved process of polymerising vinyl compounds comprises continuously forcing a solution of a vinyl compound and a catalyst through a reaction tube heated to the reaction temperature of the solution. Preferably the products leaving the reaction tube are passed through a cooling coil and drawn off as desired, and the rate of flow of the solution through the reaction tube may be controlled by the rate of drawing off the products.

It will be apparent that the temperature, pressure and rate of flow through the tube may vary according to the vinyl compound treated but it is essential, in accordance with the invention, for the polymerisation of the vinyl compound to be effected under continuous movement of the compound. By so doing products are obtained which are free from objection-

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able discolouration and, generally speaking, a higher yield of polymer is obtained.

We are aware that it has been proposed to react acetylene and hydrochloric acid gas in a reaction tube heated to the desired temperature to form vinyl chloride; and in which the flow of the gases is regulated by a suitable valve so as to maintain the desired pressure while permitting continuous operation, but such a process is obviously different from that forming the subject matter of this invention since here we carry out the polymerisation of a vinyl compound in liquid phase and there is no immediate connection between the formation of the parent vinyl compound itself and the formation of its polymers, although it is stated that in producing vinyl chloride in the continuous manner above referred to, certain polymerisation by-products may be obtained.

In carrying this invention into practice the products leaving the reaction tube are drawn off through a carefully regulated needle-valve so that the rate of flow through the tube is regulated by the rate of draw-off through the valve.

An example will now be given showing the production of a polymer of vinyl chloride:

#### EXAMPLE 1.

A 38% solution by weight of vinyl chloride in chlorobenzene containing three per cent. by weight of benzoyl peroxide, based on the vinyl chloride, was forced under 200 pounds pressure through a one-inch diameter tin-lined reaction tube having a volume of 800 cc., at the rate of 800 cc. per hour. The reaction temperature averaged 118° C. The product was a light yellow coloured solution of a new polymer of vinyl chloride. Twenty-eight per cent. of the vinyl chloride was polymerised. The new polymer is distinguished from the known polymers of vinyl chloride by reason of its solubility in toluol.

Instead of treating single polymer solutions, mixtures may be similarly treated, thus:

#### EXAMPLE 2.

A mixture of sixty parts by weight of ethyl acetate, thirty parts by weight of vinyl chloride, and ten parts by weight of vinyl acetate containing three per cent. by weight of benzoyl peroxide, based on the combined vinyl ester content, was forced through a one-inch diameter lead-lined steel reaction tube, having a volume of 800 cc., at a pressure of 200 pounds per sq. in., maintaining a temperature of 120° C. and a rate of flow of 800 cc. per hour. The interpolymerised product obtained in this manner gave a slightly

yellow solution which yielded a white polymer when precipitated with alcohol. The average yield of polymer was 66%, the concentration of vinyl chloride in the polymer being 72%.

#### EXAMPLE 3.

A solution of 1000 g. of vinyl chloride, 250 g. vinyl acetate, and 57 g. benzoyl peroxide in 650 g. ethyl acetate (63% vinyl ester concentration) was forced through a lead-line reaction tube seven-tenths of an inch in diameter and having a volume of 110 cc., under a pressure of 500 pounds at a rate of approximately 300 cc. per hour. The average temperature was 118° C. The product had a light yellow color and was quite viscous. The yield of polymer ranged from 64 to 72%, the concentration of vinyl chloride in the polymer being 80 per cent.

Since the products of Examples 2 and 3 are interpolymers it is not known whether or no the vinyl chloride polymerises under such conditions into the known alpha modification or into the new toluene-soluble modification. In any case, the products are free from objectionable discolouration.

Other vinyl compounds than esters may be similarly polymerised:

#### EXAMPLE 4.

A 45 per cent. solution of vinyl benzene (styrene) in ethyl benzene to which had been added three per cent. by weight of benzoyl peroxide, based on the styrene content, was forced through a lead-lined tube, seven-tenths of an inch in diameter and having a volume of 110 cc., under a pressure of 200 pounds, and at a rate of 200 cc. per hour. The average temperature was 117° C. Approximately 65 per cent. of the styrene was polymerised.

#### EXAMPLE 5.

A 45 per cent. solution of styrene in ethyl benzene was subjected to ozone treatment from an ozonizer for a period of 5 hours. The solution was forced through a lead-lined tube under conditions similar to those detailed in Example 4 above. Approximately the same percentage of meta styrene was obtained as in the preceding example.

Although the above examples are limited to the production of polymerised vinyl chloride, polymerised vinyl benzene, and interpolymers of polymerised vinyl chloride and polymerised vinyl acetate, it will be obvious that other polymerised vinyl derivatives, such as the polymerisation products of vinyl acetate, vinyl chloroacetate, and vinyl naphthalene, may be produced in a similar manner.

Likewise, instead of benzoyl peroxide and ozone other catalysts may be used, such as sodium bisulphite.

Also, we are not limited to the use of chlorobenzene, ethyl acetate and ethyl benzene as other solvents, such as acetone and toluene, may be used.

5 In the above examples we have indicated the preferred temperature range as being from 117 to 120° C., but we do not desire to be limited to these temperatures inas-  
10 much as temperatures above 80° C. are suitable, the time of heating being controlled by the rate of draw-off through the needle valve, and being continued until the desired degree of conversion is obtained. In general we have found that  
15 when using tubes of small diameter we may run at rates greater than the volume of the tube per hour.

It will therefore be apparent that we have developed a new and useful continuous flow process of polymerizing vinyl derivatives which permits the obtaining of higher yields of polymer; permits a definite control of the temperature of the reaction, which is difficult to control in  
25 batch processes, with a resulting likelihood of spoiling the usefulness of the resulting polymer, as by unduly darkening it; permits greater safety in operation; permits the use of highly desirable catalysts, such as benzoyl peroxide, which  
30 are unstable and whose catalytic activity would therefore be impaired at higher temperatures; and permits lower equipment and operating costs.

35 The continuous flow process disclosed herein also permits the maintenance of a high concentration of the unpolymerized ester in the liquid phase, which has been found to be particularly desirable when  
40 polymerizing vinyl chloride, either alone or in a mixture with other vinyl compounds. Vinyl chloride is apparently only slightly soluble in organic solvents at 90—120° C. and, since polymerization takes  
45 place only in the liquid phase, it is necessary to maintain the concentration of the vinyl chloride in the solution by employing excessive pressure.

When polymerizing two vinyl derivatives in mutual contact we have found that the resulting polymers are different from mixtures of the two esters polymerized  
50 separately, and the process set forth herein also permits a close control over the ratios of the two vinyl derivatives since there  
55 is no free space for the escape of one of the reactants.

Although the reaction tube is indicated in the above examples as being tin lined  
60 or lead lined steel tubing, it will be apparent that other types of reaction tubes may be used, and that the heating may be conducted electrically or in any other well known manner, and the various parts  
65 of the apparatus can be connected in any

suitable manner, as for instance with high pressure steel tubing.

Although the use of ozone as a catalyst is disclosed herein, it is not claimed broadly in this application inasmuch as it  
70 forms the subject matter of my copending application No. 28,826/29 filed of even date herewith (Serial No. 319,587).

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to  
75 be performed, we declare that what we claim is:—

1. An improved process of polymerising vinyl derivatives, which comprises  
80 continuously forcing a solution of a vinyl compound and a catalyst through a reaction tube heated to the reaction temperature of the solution.

2. An improved process according to  
85 Claim 1 in which the rate of the drawing off of the reaction products is employed to regulate the rate of flow of the solution through the tube.

3. An improved process according to  
90 Claims 1 or 2 in which the solution passes through the tube at a rate at least as great as the volume of the tube per hour.

4. An improved process according to  
95 any one of the preceding claims in which the solution is passed into a cooling coil prior to being drawn off.

5. An improved process according to  
100 any one of the preceding claims in which the solution is a solution of vinyl chloride in an inert solvent.

6. An improved process according to  
105 any one of the preceding claims 1 to 4 in which the solution comprises one or more vinyl esters, such as vinyl acetate or vinyl chloracetate, or a hydrocarbon such as vinyl benzene or vinyl naphthalene, with or without vinyl chloride in  
110 admixture.

7. An improved process according to  
Claims 5 to 6 in which the catalyst employed is benzoyl peroxide, ozone, or sodium bisulphite.

8. The process of preparing a polymer  
115 of vinyl chloride substantially as set forth in Example 1.

9. A polymer of vinyl chloride whenever prepared or produced by the process  
120 according to Example 1.

10. The improved processes of preparing polymers of vinyl compounds substantially as set forth with reference to the  
Examples 2 to 5.

11. Vinyl compound polymers whenever prepared by the special processes  
125 hereinbefore described and claimed.

Dated this 23rd day of September, 1929.  
MARKS & CLERK.